

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-118428

(43)Date of publication of application : 27.04.2001

(51)Int.Cl.

H01B 3/30
C08L 23/00
C08L 77/00
C08L101/16
H01B 3/44

(21)Application number : 11-296488

(71)Applicant : EMUSU SHOWA DENKO:KK

(22)Date of filing : 19.10.1999

(72)Inventor : NAKAMURA JUNICHI
TAMURA TAKASHI
INOUE HIROFUMI

(54) ELECTRIC WIRE-COATING RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an electric wire-coating resin composition having an excellent appearance and a solid surface.

SOLUTION: An electric wire-coating resin composition of the present invention contains (A) 100 parts by weight of a thermoplastic resin, and (B) 0.5 to 30 parts by weight of organophilized layered silicates uniformly dispersed in the resin.

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1](A) A wire coating resin composition containing (B) parent organic matter-ized sheet silicate 0.5 distributed to thermoplastics 100 mass part and homogeneity - 30 mass parts.

[Claim 2]The wire coating resin composition according to claim 1 whose thermoplastics is polyamide resin.

[Claim 3]The wire coating resin composition according to claim 1 or 2 whose thermoplastics is the polyamide 12.

[Claim 4]The wire coating resin composition according to claim 1 whose thermoplastics is polyolefin system resin.

[Claim 5]The wire coating resin composition according to claim 2 which is the triazine-ized sheet silicate from which a parent organic matter-ized sheet silicate has incorporated a triazine compound derivative which has at least one positive charge between layers.

[Translation done.]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to appearance and the wire coating resin composition in which surface stiffness is excellent.

[0002]

[Description of the Prior Art]The damage of an open circuit or fault current in which, as for the cable, the operating environment made an ant, a rat, etc. the cause in recent years depending on the place which becomes severe and is used poses a problem. It is effective to use the material which raised surface stiffness as a measure for these problems, glass fiber is added to the thermoplastics which is resin for wire coverings, such as VCM/PVC system resin and polyolefin system resin, and there is an improved method, such as hardening the surface.

[0003]

[Problem(s) to be Solved by the Invention]However, in order for the resin which added the above-mentioned glass fiber to take out appearance not only worsening but an effect, it had the problem that a lot of glass fibers were needed. This invention makes it a technical problem to provide the constituent for wire coverings which is made in view of this situation, is excellent in appearance, and is moreover excellent in surface stiffness.

[0004]

[Means for Solving the Problem]As a result of repeating research wholeheartedly about a wire coating resin composition which is excellent in appearance and is moreover excellent in surface stiffness, this invention persons find out that the above-mentioned problem is solvable with resin which made thermoplastics distribute a little parent organic matter-ized sheet silicates uniformly in comparison, and come to complete this invention.

[0005]namely, this invention -- (A) thermoplastics -- a wire coating resin composition which contains (B) parent organic matter-ized sheet silicate 0.5 distributed uniformly - 30 mass parts 100 mass part is provided.

[0006]

[Embodiment of the Invention]If it is a resin material used for a wire covering as thermoplastics used by this invention, there will be no restriction in particular and polyolefin system resin, polyamide resin, polyvinyl chloride system resin, etc. will be mentioned.

[0007]As polyolefin system resin, concretely Polyethylene, polypropylene, The homopolymer;1-butene of the olefin of polybutene and Polly 4-methylpentene-1 grade, Alpha olefins, such as 1-hexene and 1-octene, ethylene, or a copolymer with propylene, The copolymer of olefins, such as ethylene propylene rubber, and alpha olefin; Ethylene, Olefins, such as propylene, a maleic anhydride, itaconic acid anhydride, anhydrous citraconic acid, And a copolymer with unsaturation dicarboxylic anhydrides, such as a bicyclo[2,2,1]-hept 5-ene- 2,3-dicarboxylic anhydride; An ethylene-(meta) acrylic acid copolymer, Unsaturated carboxylic acid with ethylene or copolymers with unsaturated carboxylic acid ester, such as an ethylene-(meta) acrylic ester copolymer; ethylene system ternary polymerization objects, such as an ethylene-(meta) acrylic ester maleic

anhydride copolymer, etc. are mentioned.

[0008]As a copolymerization ratio of the above-mentioned unsaturation dicarboxylic anhydride, it is usually 0.5 to 5 mass %, and is 1.0 to 4 mass % preferably. the copolymerization ratio of the above-mentioned unsaturated carboxylic acid ester -- at most 20 mass % -- it is below 15 mass % preferably.

[0009]What is produced by carrying out the graft polymerization of said unsaturation dicarboxylic anhydride to the above-mentioned polyolefin system resin is used suitably. the amount of grafts of an unsaturation dicarboxylic anhydride -- 0.01 to 5 mass % -- it is 0.05 to 4 mass % preferably. The graft method can use a publicly known method, for example, the method of carrying out melt kneading of polyolefin system resin and the unsaturation dicarboxylic anhydride with an extrusion machine under existence of organic peroxide, the method of making it react in a solution, etc.

[0010]Although polyamide resin is a high molecular compound which generally has acid amide bonds ($-\text{CONH}-$) in a repeating unit and it is not limited in particular, as an example of representation, The polyamide from the lactam or omega-amino acid of the polyamide 6, the polyamide 11, and polyamide 12 grade. The polyamide from the dicarboxylic acid and diamine of the polyamide 66, the polyamide 610, the polyamide 612, and polyamide 46 grade. The copolymerization polyamide of the polyamide 6-66 and polyamide 6-610 grade. Aromatic dicarboxylic acid and aliphatic diamine, such as terephthalic acid (T) of the polyamide 6T, the polyamide 6I, the polyamide 6T/6I, and polyamide MXD6 grade, and isophthalic acid (I), Or the semi aromatic polyamide which are chosen from aromatic diamine and aliphatic dicarboxylic acid, such as m-xylylene diamine (MXD), is mentioned. The polyamide from lactam or omega-amino acid is [among these] preferred, and the polyamide 12 is more preferred at the point of excelling in extrusion-molding nature.

[0011]Polyvinyl chloride system resin is copolymerization of the monomer of the other type which can carry out copolymerization of the VCM/PVC to homopolymerization or VCM/PVC, and VCM/PVC. As an example of representation of the monomer of other type, a vinylidene chloride, ethylene, vinyl acetate, acrylonitrile, acrylic acid (meta), maleic anhydrides, or those ester is mentioned.

[0012]These thermoplastics may be independent or may use two or more kinds together. Also in these thermoplastics, polyolefin system resin and polyamide resin are used preferably.

[0013]The parent organic matter-sized sheet silicate which is used by this invention and which was distributed uniformly parents-izes [organic-matter-] the sheet silicate of a mineral constituent, and flake-izes it.

[0014]The sheet silicate is rich in change, such as chemical composition and a crystal structure, and there is nothing that was established in a classification and naming. The feature of the sheet silicate said here is a lamellar crystal, and a mineralogy top belongs to phyllosilicate. There is 1:1 type phyllosilicate which consists of the 2:1 type phyllosilicate and the tetrahedral layer of one sheet which consist of a tetrahedral layer of two sheets and an octahedral layer of one sheet especially, and an octahedral layer of one sheet, There are a smectite, a vermiculite, mica, and chlorites as a typical mineral of 2:1 type phyllosilicate, and there are kaolin, Sir pen TIN, etc. in 1:1 type phyllosilicate. There are saponite, hectorite, a sauconite, montmorillonite, beidellite, nontronite, a SUTEBUN site, etc. in a smectite group, and in a vermiculite group. There are a trio KUTAHEDORARU vermiculite, a diocta HEDORARU vermiculite, etc., and constituents, such as phlogopite, biotite, lepidolite, muscovite, a palagonite, a chlorite, margarite, a TENIO light, and tetra silicic mica, are mentioned to a mica group. These phyllosilicate may be the synthetic compounds by the thing produced from nature or a hydrothermal method, scorification, a solid phase technique, etc.

[0015]As a compound for forming a sheet silicate into a parent organic matter, If it is a positive charge organic compound which has basicity, such as an organic cation and a Lewis base, it will not be limited especially as the kind, but amine compounds, such as a primary amine, a secondary amine, and a tertiary amine, an amino acid derivative, a nitrogen content heterocyclic compound, a phosphine compound, etc. are mentioned, for example. Acid and the base reactant of these compounds and Lewis acid, quarternary ammonium salt, a HOSUHONIMU salt, etc. can

be used conveniently.

[0016]Specifically Octylamine, lauryl amine, tetradecylamine, Hexadecyl amine, stearylamine, oleylamine, allylamine, Primary amines, such as benzylamine and aniline, dilauryl amine, ditetradecyl amine, Secondary amines, such as dihexadecyl amine, distearyl amine, and N-methylaniline. Dimethyl octylamine, dimethyldodecyl amine, dimethyl lauryl amine, Dimethyl Millis Chill Amin, dimethylpalmitylamine, dimethylstearylamine, Dilauryl monomethylamine, tributylamine, trioctylamine, Tertiary amines, such as N,N-dimethylaniline, tetrabutyl ammonium ion, Tetrahexylammonium ion, dihexyldimethylammonium ion, Dioctyldimethylammonium ion, hexyl trimethyl ammonium ion, Octyl trimethyl ammonium ion, dodecyl trimethyl ammonium ion, tetradecyl trimethyl ammonium ion, hexadecyl trimethyl ammonium ion, stearyl trimethyl ammonium ion, docosenyl trimethyl ammonium ion, Sept Iles trimethylammonium ion, Sept Iles triethylammonium ion, Tetradecyldimethylbenzyl ammonium ion, stearyldimethylbenzyl ammonium ion, Dioleoyl dimethylammonium ion, methyldi ethanol lauryl ammonium ion, Methyldi propanol lauryl ammonium ion, JIMECHIRUMONO ethanol lauryl ammonium ion, The quarternary ammonium salt which generates quaternary ammonium ions, such as polyoxyethylene dodecyl monomethyl ammonium ion. Leucine, cystein, phenylalanine, tyrosine, aspartic acid, Glutamic acid, lysine, 6-aminohexylcarboxylic acid, 12-amino lauryl carboxylic acid, N,N-dimethyl- 6-aminohexylcarboxylic acid, N,N-dimethyl- 10-aminodecylcarboxylic acid, Nitrogen content heterocyclic compounds, such as amino acid derivatives, such as N,N-dimethyl- 12-amino lauryl carboxylic acid, pyridine, pyrimidine, pyrrole, imidazole, proline, gamma-lactam, histidine, tryptophan, melamine, isocyanuric acid, and melamine cyanurate. Phosphine compounds, such as triphenyl phosphine, are mentioned. These positive charge organic compounds are one-sort independent, or can be combined two or more sorts and can be used. It is triazine compound which a nitrogen content heterocyclic compound is used preferably among these, and has triazine rings, such as melamine, isocyanuric acid, and melamine cyanurate, more preferably.

[0017]Lewis acid is an electron pair acceptor, for example, thio acid, such as oxo acid, such as hydro acid, such as chloride and hydrogen sulfide, sulfuric acid, nitric acid, acetic acid, and phosphoric acid, and ethylxanthogenic acid, alkyl halide, acid halide, etc. are illustrated.

[0018]More, in details, say the compound which has six membered-rings containing three nitrogen atoms, and triazine compound is a 1,3,5-triazine system compound preferably, and specifically, Melamine, such as melamine, N-ethylene melamine, and N,N',N''-triphenylmelamine. Cyanuric acid, isocyanuric acid, trimethyl cyanurate, the Tori (n-propyl) cyanurate, The melamine cyanurate which consist of an equimolar reactant with cyanuric acids, such as tris (n-propyl) isocyanurate, diethyl cyanurate, N,N'-diethyl isocyanurate, methyl cyanurate, and methyl isocyanurate, and melamine and cyanuric acids is mentioned. A melamine cyanurate compound mixes the solution of melamine, and the solution of cyanuric acid, for example, and at the temperature of about 90-100 **, a stirring reaction can be carried out and it can obtain them.

[0019]With the triazine compound derivative which it has at least one, the positive charge used for this invention. After dissolving triazine compound which is triazine compound and a reactant of Lewis acid and is a base as a method of obtaining this in water or alcohol, it adds, and Lewis acid can be stirred and can be obtained by the method of carrying out acid and a base reaction. As an addition of Lewis acid, it is usually 0.01-3 mol to 1 mol of triazine compound, and 0.1-2 mol is more preferred. Although the generated triazine compound derivative can be used also in the state of a solution as it is, even if it takes out and uses it, it is not cared about. A commercial item can also be used making it able to dissolve in solvents, such as remaining as it is or water.

[0020]A sheet silicate and a triazine compound derivative are mixed and there is no restriction in particular about the method of obtaining the triazine-ized sheet silicate of this invention. For example, the method of carrying out mixed contact directly without using the method and medium which contact the both sides of a triazine compound derivative to a sheet silicate via an affinitive medium, etc. are mentioned. In the method of making it contacting via a medium, after distributing a solvent and making each equalize, it mixes stirring and the method of removing and obtaining a solvent is illustrated. In the method of mixing directly, the method of obtaining by putting both sides into a ball mill, a mortar, etc. simultaneously, and co-grinding them is

mentioned.

[0021]The range of 0.1–10 Eq of the amounts [0.3–10 Eq of] of positive charge organic compounds in a parent organic matter-ized sheet silicate is 0.5–2.0 Eq more preferably to the cation exchange capacity (henceforth CEC) which a sheet silicate has. If the addition of a positive charge organic compound turns into less than 0.1 Eq, the distribution to the resin composition of an intercalation compound cannot fall, and the stiffness of sufficient surface cannot be revealed. If it becomes 10 Eq or more, a positive charge organic compound will become superfluous to a mineral constituent, there is a possibility of checking the dynamic strength and the moldability of a resin composition, and it is not desirable.

[0022]Since it changes with the kind of sheet silicate, an origin, and presentations, respectively, it is necessary to measure CEC of a sheet silicate beforehand. As measurement of CEC, there are a column infiltration process (reference: the volume for "clay handbook" second-edition Clay Science of Japan, the 576–577th paragraphs, work assembly hall publication), a methylene blue adsorption process (Japanese bentonite industrial meeting standard test method and JBAS–107–91), etc., for example.

[0023]The addition of the parent organic matter-ized sheet silicate distributed to the homogeneity of the wire coating resin composition of this invention is the range of one to 20 mass part more preferably 0.5 to 25 mass part 0.5 to 30 mass part to thermoplastics 100 mass part. Less than 0.1 mass parts of an addition are [improvement of surface stiffness] insufficient, and since molding workability will be spoiled if 30 mass parts are exceeded, it is not desirable.

[0024]The sheet silicate of this invention is formed into the parent organic matter, is a manufacturing process which contacts a positive charge organic compound to a sheet silicate, and forms the intercalation compound which these at least some positive charge organic compounds inserted between the layers of a sheet silicate, and carried out the ionic bond to the silicate sheet. The check of inserting can presume the parent organic matter-ized sheet silicate of this invention a powder X diffraction (XRD) and by carrying out thermogravimetric measurement (TG/DTA).

[0025]Methods of adding the parent organic matter-ized sheet silicate of this invention to thermoplastics include methods, such as carrying out melt kneading of the parent organic matter-ized sheet silicate to thermoplastics within a melt kneading device. As an example of a melt kneading device, a continuous mixer, a Banbury mixer, a roll, a single screw extruder, a twin screw extruder, a tandem-die extrusion machine, etc. are mentioned.

[0026]To the resin composition of this invention, the additive agent of common use in this industry, for example, an anti-oxidant, fire retardant, lubricant, colorant, etc. may be added in the range which does not spoil the effect of this invention.

[0027]

[Example]Although the example of this invention is shown below, this invention is not limited to these examples.

[0028]As polyamide resin, relative viscosity (the 1 mass % polymer solution in 98% sulfuric acid was measured at the temperature of 25 **.) used the polyamide 12 (henceforth "PA-2") the polyamide 66 (henceforth "PA-1") which is 2.7, and whose relative viscosity are 2.3.

[0029]As polyolefin system resin, the polypropylene (henceforth "PO-1") as for which the 0.2 mass % graft made the maleic anhydride MFR=1g/polypropylene for 10 minutes (JIS K7210) was used. The measuring method of physical properties is as follows.

(1) Surface stiffness pencil hardness was used.

(2) Appearance viewing observation was performed.

[0030]The parent organic matter-ized sheet silicate was prepared by the following method. SC-1: It mixed in distilled water 4000mL, and 200 g of synthetic sodium 4 silicon mica (ion exchange capacity; 107 meq/100 g CO-OP CHEMICAL CO., LTD. make "SOMASHIFU ME-100") was fully swollen. These dispersion liquid were heated at 60 **, 1.0 Eq of 60 ** melamine hydrochloride solution was added to the ion exchange capacity of a sheet silicate, it fully stirred, and the ion exchange reaction was performed. This suspension was filtered, washing and filtration were repeated, it dried and ground and the triazine-ized sheet silicate was obtained.

The bottom interval of the obtained triazine-ized sheet silicate was 1.3 nm, and melamine derivative content was 10 mass %.

SC-2: In manufacture of SC-1, distearyldimethyl ammonium chloride was used instead of the melamine hydrochloride.

[0031] Each ingredient was blended by the combination shown in the one to Examples 1-5 and comparative example 4 table 1, melt kneading was carried out at 270 ** with the twin screw extruder, and the pellet was created. The plate (size; 100x100x2 mm) was fabricated for each obtained pellet using the injection molding machine. A result is shown in Table 1.

[0032]

[Table 1]

	熱可塑性樹脂		充填物		鉛筆硬度	外觀
	種類	質量部	種類	質量部		
実施例 1	PA-1	100	SC-1	3	F	○
実施例 2	PA-1	100	SC-1	7	H	○
実施例 3	PA-1	100	SC-1	15	2H	○
実施例 4	PA-2	100	SC-1	7	HB	○
実施例 5	PO-1	100	SC-2	7	2B~B	○
比較例 1	PA-1	100	—	—	HB	○
比較例 2	PA-1	100	ガラス繊維	15	H	×
比較例 3	PA-2	100	—	—	2B	○
比較例 4	PO-1	100	—	—	3B	○

[Effect of the Invention] Since the resin composition of this invention is excellent in appearance and moreover excellent in surface stiffness, it is useful as a charge of wire covering material.

[Translation done.]